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Membrane biodiesel production and refining technology: A critical review

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ABSTRACT

Membranes processes for the production and refining of biodiesel are being increasingly reported. Membrane technology has attracted the interest of researchers for its ability to provide high purity and quality biodiesel fuel besides its remarkable biodiesel yields. Membranes have numerous numbers of useful properties such as resistance to mechanical, chemical and thermal stress, high available surface area per unit volume, high selectivity, and ability to control the components contact between the two phases makes them potential. These properties have made them to be potential candidates for both upstream and downstream biodiesel production and refining applications. In this regards, this paper critically examined the production and refining of biodiesel fuel via membrane technology.

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1. Introduction

Biodiesel as a source of energy has been receiving great attention among the futurist and the world policy makers [1]. This is so because of its renewability, biodegradability, and better quality of exhaust gas emission [2]. The idea of vegetable oil based fuel to run diesel engines has been on the world stage over a century ago. The discovery of the potentials of vegetable oil to serve as fuel was made by one of the most famous scientist of the nineteenth century called "Rudolf Diesel". Rudolf Diesel, in 1912 stated that "the use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time" [3]. The interest to develop the technology of biodiesel fuel over the years was low due to availability and low cost petroleum products. The renewed and increasing interest in the growth and development of

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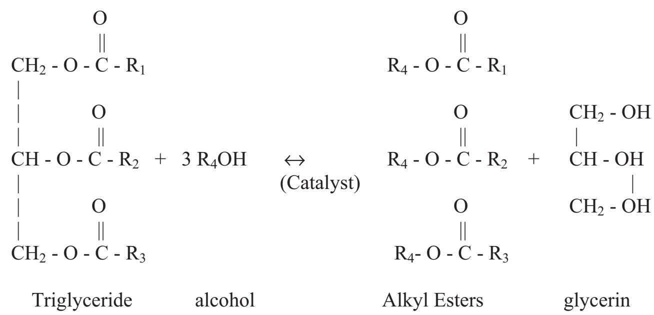

Fig. 1. Transesterification reaction of triglyceride to biodiesel.

biodiesel fuel is driven mainly by its potentials to solve three main challenges confronting the global economy. These include among others: how to attain energy independence, reduce environmental impact and achieve fuel of affordable prices that can compete favorably with the conventional diesel fuel. Thus, biodiesel fuel in large quantities could be achieved if certain technologies are developed. Some of these technologies include: (1) Establishment of a scheme to generate low cost feedstocks. (2) Development of sound technology for the purification of crude biodiesel. (3) Development of good catalysts that can give higher yields of biodiesel with less refining difficulties. (4) Establishment of a sound policy that can improve the production of biodiesel fuels. (5) Exploration and exploitation of biodiesel production systems with the aim of minimizing energy and water use [1].

Biodiesel fuel is produced via different techniques such as: direct/blends [4,5], microemulsion [6,7], pyrolysis [8,9], and transesterification [10,11]. Among these techniques, transesterification reaction is the most adopted technique used to convert fats and oils into biodiesel fuel [10,12,13]. Fig. 1 presents transesterification of tri triglyceride to biodiesel. Whereas Fig. 2 depicts the structure of triglyceride used as a feedstock to produce biodiesel fuel [14]. The process of transesterification reaction is usually catalyzed by either homogeneous or heterogeneous catalysts. The most notable catalysts are: NaOH, KOH, CH_3ONa, and CH_3OK. Recently heterogeneous catalysts such as solid catalysts ($Ca(NO_3)_2/Al_2O_3$, CaO/Al_2O_3, $Sr(NO_3)_2/ZnO$, ZrO_2/SO_4^{2-}, zeolite HY, and zeolite X) and enzymes (*Pseudomonas fluorescens*, *Rhizopus Oryzae*, *Candida rugosa* and *Pseudonas cepacia*) are applied for the production of biodiesel. In addition, feedstocks such as virgin and used oils, animal fats, and microalgal oil are used as raw materials for the production of biodiesel fuel as shown in Table 1.

Biodiesel has been conventionally produced using reactors such as batch reactors, CSTR and plug flow reactors. However, the recent introduction of membrane reactor is significant in producing biodiesel for its ability to block the passage of unreacted triglyceride to final biodiesel product. This phenomenon has the benefits of providing high-quality biodiesel fuel. This is so because

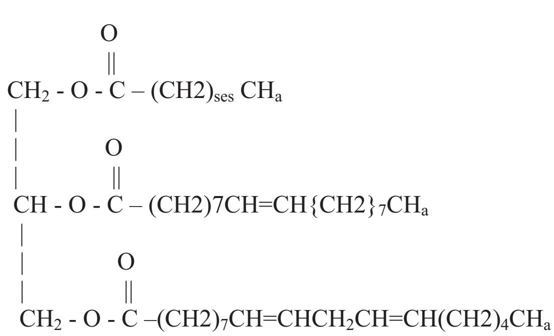

Fig. 2. Structure of typical triglyceride molecule.

Table 1
Biodiesel production through transesterification reaction.

Feedstock	Catalyst	Reference
Waste tallow (chicken)	H_2SO_4	[15]
Palm fatty acid	H_2SO_4	[16]
Waste cooking oil	ZS/Si	[17]
Soybean oil	CaO	[18]
Sunflower	Zeolite X	[19]
Refined soybean oil	Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$	[20]
Waste bleaching earths	*Rhizopus oryzae*	[21]
Sunflower oil	KOH	[22]
Jojoba oil-wax	Sodium methoxide	[23]
Brassica carinata	KOH	[24]
Canola oil	KOH	[25]
Cooking oils	–	[26]
Soybean	Na/NaOH/γ-Al_2O_3	[27]
Crude palm kernel oil	SO_4^{2-}/ZrO_2	[28]
Soybean oil	Lipase	[29]
Jatropha curcas	KOH	[30]
Cottonseed oils	Sodium hydroxide	[31]
Roselle oil	Potassium hydroxide	[32]
Rubber seed oil (*Hevea brasiliensis*)	NaOH	[33]
Mahua oil (*Madhuca Indica*)	NaOH	[34]
Mahua oil	H_2SO_4/KOH	[35]
Soybean oil	ETS-10 zeolite	[36]
Sunflower frying oil	KOH	[37]
Tobacco seed oil	NaOH	[38]
Rice bran oil	Sulfuric acid	[39]
Palm oil	CaO/Al_2O_3	[10]
Used frying oil	KOH	[40]
Waste cooking oil	H_2SO_4/NaOH	[41]
Heterotrophic microalgal oil	Sulfuric acid	[42]

unreacted triglycerides constitute one of main impurities that need to be removed after transesterification is completed.

Production of biodiesel with full conformity to biodiesel international standard specification (EN 14214) is technically difficult, especially meeting the needs of biodiesel fuel standard of biodiesel yield of 96.5 wt.% (EN 14214) [26]. The crude biodiesel product obtained from both conventional and membrane reactors comes with impurities such as glycerol, soap, residual catalyst and excess alcohol that need to be removed. Purification of crude biodiesel from these impurities is necessary so as to make biodiesel suitable for diesel engines consumption and other applications. The presence of these impurities in biodiesel fuel could cause severe engines problems and damages [43]. The removal of these impurities via conventional separation and purification techniques poses severe difficulties such as huge amount of water usage, high energy consumption, time wasting and treatment of wastewater [44,45]. This has led to the recent application of organic/inorganic separative membranes for the refining of crude biodiesel. Membrane biodiesel separation processes seem to provide high-quality biodiesel fuel [2,46,47]. Also, a large portion of membrane separation processes are carried out under moderate temperature and pressure conditions and their scale-up are less cumbersome. Furthermore, membranes are generally most preferred in the refining processes for the following reasons: low energy consumption, safety, simple operation, elimination of wastewater treatment, easy change of scale, higher mechanical, thermal and chemical stability, and resistance to corrosion [48]. Therefore, this study critically examined the production and refining of biodiesel using membrane technology.

2. Application of membranes for the production of biodiesel fuel

Membrane system exploits the inherent characteristics of high selectivity, high surface area per unit volume, and their potential for controlling the level of components mixing between the two phases [49]. The application of membranes for biodiesel production

is usually designed in two phases, one phase is the membrane reactor to transesterify fats and oils to biodiesel, and the other phase is the separative membrane to separate the crude biodiesel from its impurities such as: catalysts, soap, glycerol, and alcohol without necessarily using water, acids, organic solvents and absorbents. Membranes are usually classified into organic, inorganic or combination of the two. Organic membranes are mostly avoided for processes involving high acidic and basic environments due to their less resilience. However, inorganic membranes such as metallic, ceramic, zeolitic or carbon-made are mostly preferred because of their ability to withstand harsh conditions such as higher temperatures, high acidic and basic environments [50]. Thus the term ceramic membranes are porous fine ceramic filters sintered from aluminia or titania, zirconia oxides under ultra high temperature and usually have an asymmetrical structures with porous support active membrane layer. The macro-porous support ensures the mechanical resistance whereas the active layer allows microfiltration, ultrafiltration separation process. Also, ceramic membranes always runs at a across flow filtration mode [51]. In the cross flow mode, the fluid to be filtered flows parallel to the membrane surface and permeates through the membrane due to a pressure difference [49]. This characteristic of ceramic membranes reduces fouling effects and improve high filtration rate [51].

2.1. Issues governing conventional biodiesel production

Homogeneously catalyzed transesterification in a stirred tank reactor is most favored technique for biodiesel production [52]. Homogeneous catalysts such as NaOH, KOH, CH_3ONa and CH_3OK are well established to provide excellent catalytic activities in the production of biodiesel [53]. However issues such as difficulties in refining, cost of refining process, and waster water generation have being the major problem of this technology. Therefore to overcome these problems heterogeneous catalysts are explored and exploited, these catalysts can be easily removed with a resultant high-quality biodiesel product.

2.1.1. Types of non-membrane reactors used for biodiesel production

The non-membrane reactors that have been employed for the production of biodiesel include among others: batch reactors [54–56], plug flow reactors [57], continuous stirred tank reactors (CSTR) [16,57,58], fixed bed reactors [59–61], helicoidal reactor [62], transport riser reactor [63] and oscillatory flow reactor [64]. Using batch reactors, a good number of researchers have reported higher conversions of triglycerides to biodiesel fuel [65–67].

2.1.2. Challenges in producing biodiesel using conventional reactors

Commercial production of biodiesel fuel via batch reactors is mostly discouraged due to their tedious mode of operations. Besides, cost of biodiesel production due to labor. These problems have led to using plug flow reactors, CSTR and fixed bed reactors for the production of biodiesel. These reactors have the potentials of being used for the production of biodiesel fuels, but problems ranging from lower conversion efficiencies, difficulties in processing low quality feedstocks, mass transfer limitation [68], non-uniform product distribution, low quality biodiesel products, poor biodiesel yields, higher reaction conditions [69], labor and reactor facility degradation due to chemical attacks have discourage their commercial applicability. Helwani et al. [70] reported the main drawback of the continuous stirred tank reactors or tubular reactors is that the temperature of reaction is narrowed to the boiling point of alcohol; 65 °C for methanol, if the reactor is operate at atmospheric pressure. The authors noted that for industrial size reactor, significant mass transfer resistance is expected even when higher shear mixing is employed. These problems have eventually led to the exploration and exploitation of membrane technology for the production of biodiesel fuel. Dubé et al. [71] and Dubé [72] remarked that the technical difficulties such as immiscibility of triglycerides and alcohols and reversibility problems commonly encountered with conventional reactors can be overcome via membrane reactor.

2.2. Membrane reactor

Development of a membrane reactor and its successful application in producing biodiesel has renewed the strong interest to develop alternative renewable and sustainable fuel to replace petro-diesel fuel. Membrane reactors can serve different purposes such as intensify the contact between reactants and catalyst, selectively remove the products from the reaction mixture, and control the addition of reactants to the reaction mixture [73]. These reactors can be employed to avoid the equilibrium conversion limits of conventional reactors. Besides, the reactors can efficiently improve the maximum achievable conversion of reversible reactions and the general reaction pathways [74]. Furthermore, membrane reactors provide the potential of higher selectivities and yields in many different processes as well as being safe and more environmentally friendly [75]. Dubé et al. [71] developed a novel membrane reactor that enabled both acid- or base-catalyzed-transesterification of canola oil as well as separation of unreacted canola oil from reaction products. The membrane reactor consisted of membrane pore size of 0.05 μm, inside and outside diameters of the membrane were 6 and 8 mm, length of carbon membrane tube of 1200 mm and a surface area of 0.022 m^2. The membrane reactor was charged with canola oil (100 g) and sealed. Following circulation time of 10 min, the reactor was operated continuously at a pressure of 138 kPa with feed (mixture of methanol and acid) pump flow rate of 6.1 mL/min. The heat exchanger was switched on to achieve temperatures of reaction (60, 65 and 70 °C) which was monitored by a thermocouple. Therefore after starting the heat exchanger a stable reaction (±0.1 °C) time was achieved with 30 min for 60 °C, 40 min for 65 °C and 45 min for 70 °C. The experiments were all conducted for 6 h. The authors remarked that an additional experiment was also performed to study the effects of methanol/acid catalyst feed flow rate on conversion for both acid- and base-catalyzed transesterifications. The flow rates were 2.5, 3.2 and 6.1 mL/min. The schematic diagram of the membrane reactor is depicted in Fig. 3 [71]. Similarly, Cao et al. [69] transesterified a number of vegetable oils such as canola, soybean, palm, and yellow grease lipids via a membrane reactor. The authors noted that despite the wide range of feedstocks used, the membrane reactor presented a moderately consistent performance at one set of operating conditions and enabled the production of high-quality biodiesel fuel which was confirmed by GC analysis based on the ASTM D6584 standard. The biodiesel from all the feedstocks met the ASTM D6751 standard. Also, the glycerol content of biodiesel produced using a membrane reactor was significantly lower than that produced via a conventional batch reaction. Another study conducted by Cao et al. [76] compared three different recycling ratios for production of biodiesel via membrane reactor: 100%, 75% and 50% by volume, for instance, 75% recycling entails that every 0.75 L of polar phase was mixed with 0.25 L methanol with 1 wt% (by weight of oil) NaOH catalyst and pumped into the reactor circulating loop at a feed rate of 3 L/h, while the feed rate of canola oil was also kept at 3 L/h. The authors noted that the catalysts and glycerol were also recycled. Furthermore, to maintain biodiesel-rich non-polar phase containing 85 wt.%, the permeate was consistently removed as well as methanol/glycerol polar phase. Consequently, at maximum recycle ratio, the fatty acid methyl esters (FAME) concentration ranged from 85.7 to 92.4 wt.% was found in biodiesel-rich non-polar phase. In addition, the overall

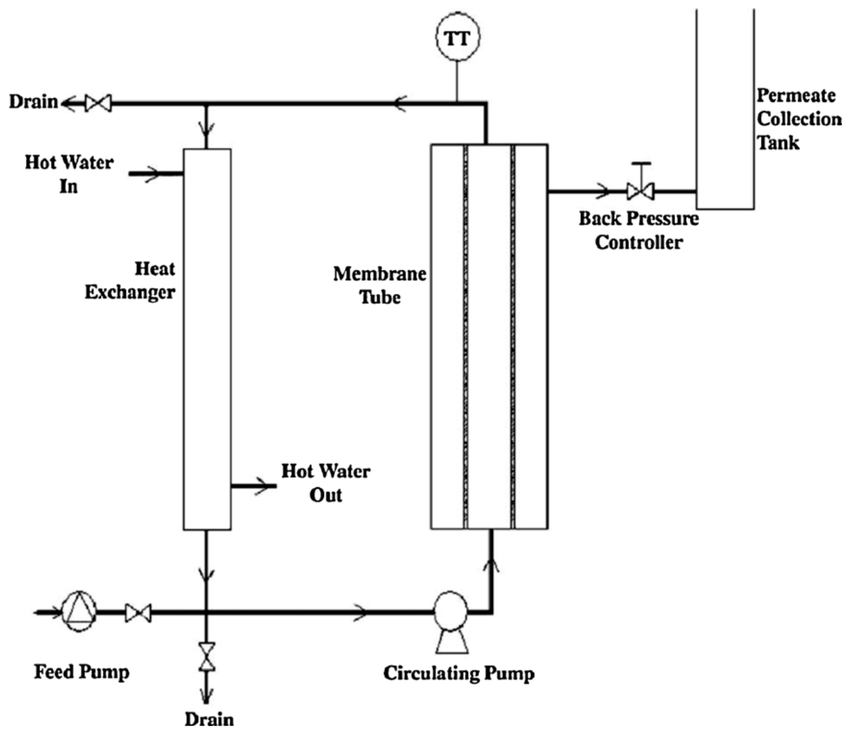

Fig. 3. Schematic diagram of biodiesel membrane reactor.

molar ratio of methanol:oil in the reaction system was significantly decreased to 10:1 while maintaining a FAME production rate of 0.04 kg/min. Also in biodiesel-rich non-polar phase no triglycerides (TG), monoglycerides (MG) or glycerol were observed. The authors noted that despite the samples not being water washed prior to analysis, high purity biodiesel product free of non-saponifiable materials was produced. As a result, a high purity biodiesel product was produced. Although the yield obtained via homogeneous catalyst in membrane reactor was below EN14214 standard [69]. Therefore, to circumvent the problems associated with use of homogeneous catalyst, which despite use of membrane reactor still poses difficulties. Baroutian et al. [52] developed a novel continuous packed bed membrane reactor (a tubular ceramic (TiO_2/Al_2O_3) membrane) to produce biodiesel fuel using solid alkaline catalyst (potassium hydroxide catalyst supported on activated carbon). The membrane reactor comprised; length, inner diameter, outer diameter and pore size of the membrane 40 cm, 1.60 cm, 2.54 cm and 0.05 μm, respectively. The filtration surface area for the entire membrane was 0.0201 m^2. Three digital Masterflex L/S peristaltic pumps were employed to feed the raw materials and to prepare circulation inside the system. The Chem-Durance chemical resistant pump tubing with a size of 16 (ID = 44 mm, OD = 2.36 mm) was also used. The temperature and pressure were monitored via pressure gauges and temperature indicator. The authors noted that during transesterification the membrane reactor was able to block the triglycerides, but biodiesel and by-product glycerol alongside methanol passed through the membrane pore size due to their smaller molecular sizes. As discussed earlier the ability to block the triglycerides provided high-quality biodiesel fuel. Conversion of 94% was obtained at 70 °C reaction temperature, 157.04 g catalyst per unit volume of reactor and 0.21 cm/s cross flow circulation velocity. The characteristics of the product under the optimum condition were within the ASTM standard.

2.2.1. Membrane reactor operation

The term membrane reactor is usually referred to a system in which membranes separation and chemical reactions are combined. It is an appliance use to simultaneously carry out a reaction and a membrane-based separation in the same physical enclosure [77]. During chemical reaction, the immiscibility of the reactants (alcohol and fats or/and oil), is slightly affected by temperature, thus the two phases are usually considered to be immiscible. Lack of miscibility of the reactants is the root of mass transfer problems faced during biodiesel production. In membrane reactor operation, a two-phase emulsified system formation is the exact thing that is required. The two-phase membrane reactor was mainly useful in removing unreacted canola oil from the FAME product. This phenomenon has been remarkable in shifting the reaction equilibrium to the product side and yielding high purity and quality biodiesel fuel [69,71,77]. Thus, the transesterification of triglyceride to fatty acid alkyl esters is suitable to operate in a membrane reactor. Also due to various surface forces and lack of miscibility of vegetable and alcohol, oil mostly exists as an emulsion. Thus, transesterification could be envisaged to occur at the surface of oil droplet. The occurrence of a permeable membrane consisting of smaller pore sizes normally blocks the larger oil droplets. However, the solubility of fatty acid alkyl esters (FAAE) in alcohol and its smaller molecular size enables the FAAE and glycerol, catalyst and alcohol to permeate through membrane pores. Additionally, because of the reversibility of transesterification, boosting FAAE production needs the removal of either FAAE or glycerol to move the equilibrium to the product side (in accordance with Le Chatelier's Principle) [52,71].

2.2.1.1. Characteristics of membrane. Dubé et al. [71] stated that the life of membrane used in the reactor is most significant when dealing with high acid or base catalyst concentration. The authors noted that the carbon membrane resisted the high acid and base environments. They reported that membrane reactors can have several advantages over conventional reactors such as resistance to corrosion. Also, Barredo-Damas et al. [78] stated that ceramic carbon membranes offer many advantages over polymeric membranes such as high chemical, mechanical and thermal resistance to degradation and show higher permeability rates. The authors noted that

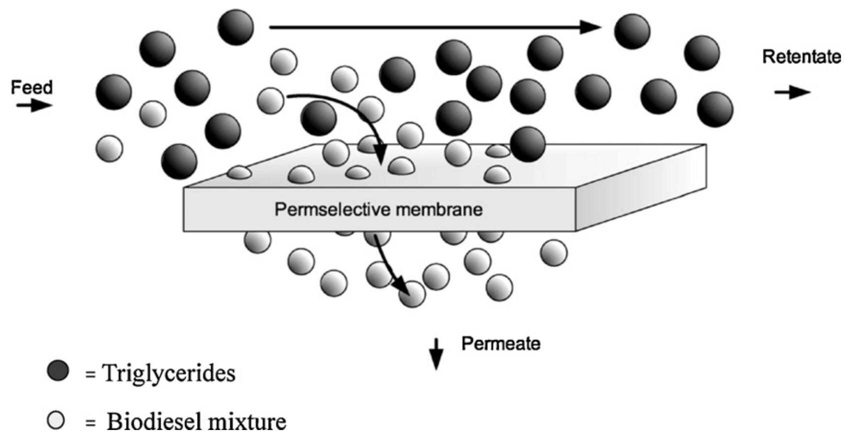

Fig. 4. Cross flow filtration configuration.

the cost of ceramic carbon membranes is being recently decreased. According to Brunetti et al. [79] membrane technology offers fundamental engineering and economic advantages over competing separation technologies. Therefore the ability to withstand the reaction conditions, chemical and thermal stabilities also allow the ceramic carbon membrane to be cleaned more proficiently when unrefined feedstocks such as used/waste cooking oils are employed [69]. Baroutian et al. [52] observed that the performance of ceramic used was not affected after operating the membrane in a reaction media containing methanol and solid alkaline catalyst for 1 year, this due to its excellent chemical and physical stability. Salahi et al. [10] stated that membrane structure has an important influence in improving permeate flux.

2.2.1.2. Effects of membrane pore size. The membrane pore size is significant in realizing high purity and quality biodiesel, since separation of crude biodiesel is to some extend dependent on the molecular size of the constituents comprising biodiesel mixture. Cao et al. [77] found out the use of four carbon membranes having different pore sizes of 0.05, 0.2, 0.5, and 1.4 μm, with four different initial methanol volume fractions of 0.29, 0.38, 0.47, and 0.64 to produce biodiesel fuel. The authors reported the canola oil used was retained by all the four membranes in the reactor. As discussed earlier retaining oils by membrane system served to provide better quality biodiesel fuel to be efficiently used in compression–ignition engines as shown in Fig. 4 [1].

2.2.1.3. Effects of catalyst. Catalysts are of great importance during transesterification triglycerides to biodiesel, in that they improve reaction rates [26]. Dubé et al. [71] employed base- and acid-catalyzed transesterification reaction to convert canola oil to biodiesel via membrane reactor. Catalyst concentration of 1 wt.% NaOH was used at different flow rates. Both homogeneous base catalyst and heterogeneous base catalyst provided high conversions compared to the acid-catalyzed process as shown in Table 2. For the base catalyzed process, little amount of soap was formed, which was detected during water washing [71]. The authors noted that the canola oil might have contained considerable amount of FFAs which most have being transformed to soap instead of biodiesel during base-catalyzed process. On the other hand no soap was formed for acid catalyzed process. Therefore acid catalyst will present both economical and technical advantage, despite slower rate of reaction when low quality feedstocks are used for the production of biodiesel [80]. However, to overcome problems associated with homogeneously catalyzed process via membrane reactor, Baroutian et al. [52] have experimented use of heterogeneous alkaline catalyst in packed bed membrane reactor. The authors employed a tubular ceramic (TiO_2/Al_2O_3) membrane as a reactor and separator, which was filled with potassium hydroxide catalyst supported on activated carbon KOH/AC. The catalyst was reused severally, and after each run the catalyst was removed, dried and reutilized. The catalytic activity remains 89.3% of the fresh catalyst when the activated carbon supported catalyst was employed for the third time. The catalytic decay could be due to leaching of the active site into reaction media. The authors noted the active site phase leaching into the alcoholic phase might be as a result of bond breaking and formation of K^+ and CH_3O^-.

2.2.2. Performance of membranes

The overall membrane performance is strongly dependent on the membrane selectivity [81]. Mahua [82] noted that membrane performance is mostly affected by several numbers of parameters such as; membrane composition, temperature, pressure, velocity of flow, and interaction between components of the feedstocks with the membrane surface. Similarly, Petr and JirÏ [83] stated the performance of membrane separation process can be characterized by permeate flow rate yielded by a given membrane device which can be, in the simplest case, calculated by the product of constant permeate flux and total filtration area. Also, Ahmad et al. [84] reported the higher the selectivity factor the better the membrane performance. They noted that selectivity factor sometimes is independent of temperature but dependent on the nature of material used in the membrane preparation. In addition, higher temperature does not necessarily produce higher selectivity. The authors stated that extensive researches must be carried out in the near future using various types of materials to form membrane with better selectivity

Table 2
Effect of flow rate on conversion using membrane reactor.

Expt.	Flow rate (mL/min)	Temperature (°C)	Conversion via acid-catalyst (%)	Conversion via base-catalyst (%)	Conversion via heterogeneous catalyst	Reference
–	–	70	–	–	94	[52]
1	2.5	65	35	95	–	[71]
2	3.2	65	48	96	–	[71]
3	6.1	65	64	96	–	[71]

factor. In another study, Saracco et al. [50] noted a change in interest from improving the equilibrium limited reactions through membrane separation of one of the products, to selectivity increase through membranes. Additionally the retention coefficient for the oil or FFAs (%*R*) can be calculated as:

$$\%R = \frac{(C_{\rm al} - C_{\rm per}) \times 100}{C_{\rm al}}$$

where $C_{\rm al}$ and $C_{\rm per}$ are the concentration of those components, in the feed and permeate respectively [85].

2.2.3. Conversion of triglycerides to biodiesel product using membrane reactor

Higher conversions/selectivities of membrane processes are usually achieved via selective removal of products or controlled and spatially distributed supply of reactants [86]. Christine and Gonzalez [87] stated that membranes can be used in reactions to improve conversion or selectivity. Cao et al. [69] reported that if the residence time or catalyst concentration is increased, conversion will increase, which increases the concentration of FAME in the reactor. However, lowering the catalyst concentration and/or decreasing the residence time can reduce the FAME concentration and prevent the occurrence of diglyceride (DG) in permeates. The authors also noted that when the FAME concentration is higher than 35 wt.% in the permeate stream, the diglyceride will solubilized into the permeate stream. They stated that after recycling, the average diglyceride concentrations in the FAME-rich non-polar permeate phase were 0.34, 0.34, and 0.32 wt.% for the 100%, 75% and 50% recycle ratio cases, respectively [76].

2.3. Prospects and challenges of producing biodiesel using membrane reactor

The use of membrane technology to produce biodiesel has shown promise in providing biodiesel whose physicochemical properties is comparable to those of petro-diesel. This is certainly a positive step in the development of biodiesel fuel for future application. Additionally, the use membrane reactor is solidly aimed to overcome problems associated with conventional reactors, which has being demonstrated in their works [52,71,88]. However, several issues are still yet to be resolved. Thus, Table 3 presents prospects and challenges of using membrane reactors for the production of biodiesel fuel.

3. Membrane biodiesel refining technology

3.1. Conventional refining technology and its challenges

After transesterification reaction, biodiesel is first separated from glycerol before being subjected to other refining processes. The separation of biodiesel from by-product, glycerol is usually fast due to difference in their densities. This separation process is usually performed by either decantation or centrifugation [92]. Other separation process includes gravitational settling [15], filtration [47], and sedimentation [93]. In decantation separation technique, the mixture of biodiesel and glycerol is rested in the tank. Although the cost of separation is low, however the process is slow and inefficient [90]. On the other hand, separation via centrifugation requires that the mixture of biodiesel and glycerol be fed into centrifuges for separation process to occur. The process of separation is fast, but its cost of operation and investment are considerably high [2,90,92].

Following removal of glycerol, biodiesel is further purified to remove impurities such as tri-, di-, and monoglycerides, catalyst, soap and traces of alcohol [93,94]. The removal of these impurities is essential so as to produce biodiesel that conform to international standard specifications (ASTM 6751-3 and EN 14214) as shown in Table 4 [26]. This is because presence of these impurities poses great impact on the purity and quality of biodiesel as fuel for use in compression–ignition engines [95].

Conventionally, purification of biodiesel is done via alcohol removal using vacuum distillation or flash evaporation, and wet or dry washings to remove triglycerides, catalyst, and soap [96]. Wet washing technique is done in several ways; it could be distilled water washing alone, washing with acids then followed by washing with distilled water or washing with organic solvent followed by washing with water. Even though, the process provides biodiesel that can be conveniently used in diesel engines. But the process is known for huge water consumption, large wastewater discharges, huge amount of energy need, high cost of wastewater treatment and drying of final biodiesel products [96]. Fig. 5 depicts conventional schematic diagram for fatty acid alkyl esters (biodiesel) production and purification. Thus, wet washing process is disliked for its significant and intolerable negative contributions to environmental pollution and degradation. Presently, concern of large amount of biodiesel contaminated wastewater disposal is rising in Thailand [45].

Furthermore, problems associated with wet washing have led to the introduction of dry washing process to purify crude biodiesel. This process involves the use of absorbent such as carbon, silica, bleaching clay, and activated bleaching clay, zeolite, ion exchange

Table 3
Presents prospects and challenges of using membrane reactors for the production of biodiesel fuel.

Prospects	Challenges
Membrane reactor	
Generation of high-quality biodiesel fuel [52,71]	High expectation for membranes systems [89]
Can be operated continuously [69]	Membrane systems are limited by pore size and shape of materials to be filtered [91]
Can process low quality feedstocks [69]	Soap formation when homogeneous alkaline catalyst is used, acid catalyzed reaction rate is slow [71]
Can combine both reaction and separation Simultaneously, acid catalyst can provide both technical and economical advantages over alkaline Catalyst when process low quality feed [71]	Leaching of solid alkaline catalyst [52]
Can effectively block unreacted triglycerides [52,69]	Previous studies have focused on the use of ceramic membranes, but these are very expensive for the targeted applications and separation performance has often been poor [90]
Easy product removal during transesterification reaction [73]	Yield are lower compared to those obtained heterogeneous catalyst in batch reactors [54]
Principally striking at eco-compatibility because they do not need additives, can run at moderate reaction condition (temperature and pressure), and can reduce forming of by-products [89]	
Replacement of centrifuge/settling tank as phase separation medium, improving the efficiency of hot water washing step [90]	

Table 4
International biodiesel standard specifications.

Properties	Units	ASTM method	EN14214
Ester content	% (m/m)	–	96.5
Flash point	°C	130 min.	>101
Water and sediment	vol.%	0.050 max.	0.05
Kinematic viscosity, 40 °C	mm^2/s	1.9–6.0	3.5–5
Sulfated ash	% (m/m)	0.020 max.	0.02
Sulfur	mg/kg	–	≤10
S 15 grade	ppm	15 max.	–
S 500 grade	–	500 max.	–
Copper strip corrosion	Rating	No. 3 max.	Class 1
Cetane	–	47 min.	≥51
Cloud point	°C	Report	–
Carbon residue 100% sample	% (m/m)	0.050 max,	–
Acid number	mg KOH/gm	0.50 max.	0.50 max.
Free glycerin	% (m/m)	0.020 max	0.02 max.
Total glycerin	% (m/m)	0.240 max.	0.25 max.
Phosphorus content	mass%	0.001 max.	0.001 max.
Distillation temperature, atmospheric equivalent temperature, 90% recovered	°C	360 max.	–
Sodium/potassium	ppm	5 max. combined	5 max.

Max.: maximum; min.: minimum.

resins (amberlite or purolite), cellulosics or sawdust, diatomaceous earth and magnesium silicate powder (magnesol or trisyl). Though the dry washing technique is remarkable for its being waterless process [97], reducing the risk of environmental contamination, decreasing energy and huge water needs. The process is capitally intensive since extra mixing unit is needed beside non-reusability of spent absorbent. It could be also added that up till now understanding of the chemistry of absorbents is skeletal [96,98], even though high-quality biodiesel fuel [99] with biodiesel yield of 98.5 wt.% [98] can obtained via the process. Besides, Berriosa and Skelton [96] found that both magnesol and ion exchange resins have no any significant effect on glycerides and therefore none of the refining process fulfilled the limit in the EN 14214 standard.

Thus, problems associated with both conventional biodiesel separation and purification processes have resulted to the exploration and exploitation of membrane technology to separate biodiesel product from impurities.

3.2. Biodiesel membrane separation processes

Membranes are selective either by pore size (porous membrane) or because of their chemical affinity for permeating component [100]. Ceramic membrane biodiesel separation and purification technology is fast growing due to their stability in organic solvents [101]. Hua et al. [102] noted that over the last 30 years, membrane separation processes have enjoyed great popularity and is

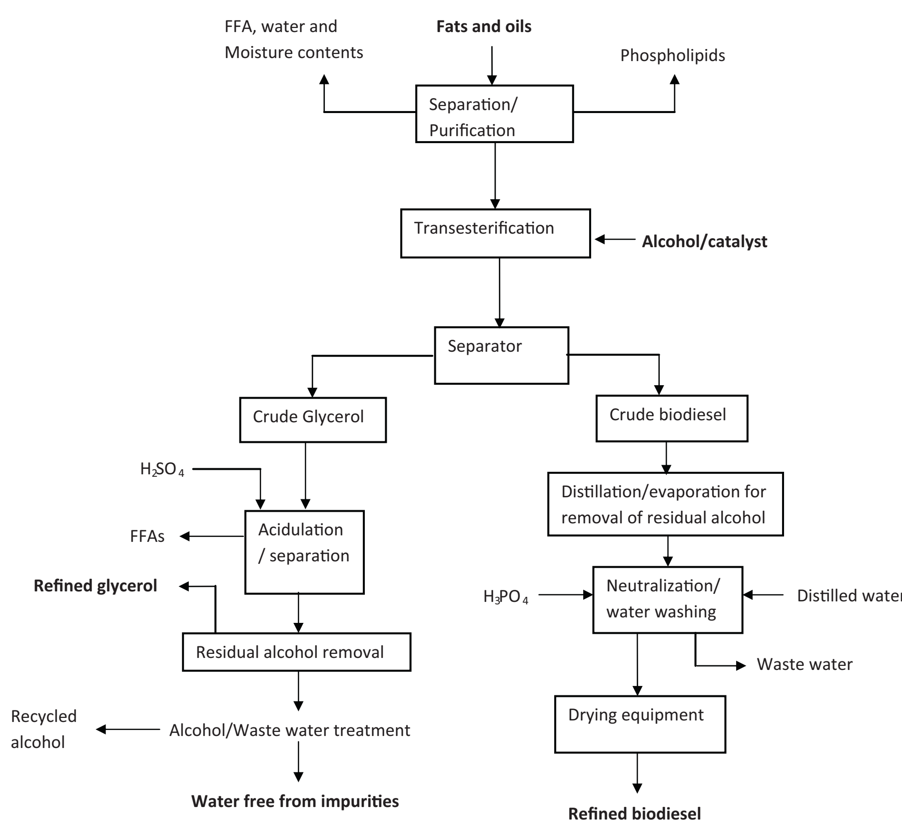

Fig. 5. Conventional schematic diagram for fatty acid alkyl esters production and purification.

widely becoming a promising technology. This is due to stable effluent quality, small area and zero chemicals needs. Besides, simple implementation of membrane scale-up [48].

The introduction of membrane technology in the field of biodiesel production technology is remarkable in that both organic and ceramic membranes have shown high prospects for the refining of crude biodiesel products [103]. Benítez et al. [104] reported that pressure-driven membranes techniques provide permeate of great quality. Dubé et al. [71] showed that a membrane reactor can be used to successfully separate crude biodiesel from unreacted vegetable oils. This separation process type can ease the difficulties faced in using conventional separation techniques in separating FAAE from vegetable oils. Alicieo et al. [105] reported that membrane technology can be useful to industries in simplifying the entire separation process, reducing energy consumption and decreasing wastewater production. It is also worth mentioning, the significant reduction in energy cost associated with membrane processes [106–108]. As an added advantage, one is required to consider the total adequacy of this new technology to environmental and safety issues, since explosion risks, for example, are minimized [85]. Membrane separation process is usually classified based on the size range of material to be separated and driving force used for the separation. This separation process is mainly a size-exclusion-based pressure-driven process [106]. The two most often used membrane processes for the separation of crude of biodiesel are the micro-filtration and ultra-filtration [49]. Paris et al. [109] noted that ultra-filtration (UF) is a pressure-driven membrane separation process used to separate different molecules in a liquid mixture.

Furthermore, membrane processes have shown some promise in the removal of contaminants such as unreacted triglycerides [69,71], catalyst [2], glycerol [92,110], soap [2], and methanol [100].

3.2.1. Biodiesel separation through ultra-filtration process

In comparison to the conventional treatments, ultra-filtration method is environmentally friendly and the separation process of contaminants from crude products is economical [111,112]. Li-Hua et al. [113] investigated a membrane separator integrated with liquid–liquid extraction for the oil–FAME–MeOH system and obtained biodiesel of high-purity. The analysis of biodiesel used showed that the actual methyl oleate (C18:1) content was 58.89 wt.%, and the overall content of C (C16:0–C18:3) was 98.68% with TG, DG, MG and free fatty acids of 0.017%, 0.029%, 0.037% and 0.376%, respectively. The ultrafiltration membrane process system employed for the refining is shown in Fig. 6. The experiments were conducted in a total recycle mode at 20 °C, 40 °C, 60 °C, and at transmembrane pressure range of 0–1000 mmHg. After the permeate began to be collected, each run took another 60 min for its completion. At first, the ultrafiltration experiments were conducted at three transmembrane pressures (600 mmHg, 500 mmHg and 400 mmHg) and three feed flow rates (300 mL/min, 400 mL/min and 500 mL/min). Furthermore, the runs were performed over a range of composition of oil:FAME:MeOH (20:30:50 wt.%, 20:40:40 wt.%, 20:65:15 wt.% and 20:75:5 wt.%) at the constant transmembrane pressure and the feed flow rate. The samples of permeates were taken every 10 min and the compositions of permeate and retentate were examined. The authors demonstrated that a two-phase system is necessary for the successful operation of the membrane separator for biodiesel purification. They further stated that the TG-free permeate obtained was as a result of the feed bulk concentration being controlled within two-phase zone such as oil:FAME:MeOH of 20:30:50 wt.%, FAME (fatty acid methyl esters) and the methanol content of the permeate were about 14 wt.% and 85 wt.% respectively, regardless of the operating pressure and the cross flow rate.

Furthermore, He et al. [46] have compared the conventional biodiesel refining techniques and hollow fiber membranes such as polyacrylonitrile and polysulfone. The authors noted membrane refining technique to overcome forming emulsion of water and the esters, decrease purification losses in comparison to the conventional techniques and provide biodiesel purity of 99 wt.%. Saleh et al. [47] studied the ability of membrane processes to remove free glycerol particles from FAME, without using a water wash step, as well as, the effect of different materials such as water, soap, and methanol on the final separation performance. Modified polyacrylonitrile (PAN) membrane; with 100 kD molecular weight cut-off were employed in all the runs to remove free glycerol from biodiesel which was conducted at temperature of 25 °C and pressure of 552 kPa. For FAME only the removal of glycerol via membrane was extremely hard. Consequently different percentages of water, methanol and soap were added to FAME to facilitate the eradication of glycerol. For FAME containing 1% methanol, the separation was very low indicating that methanol does not lead to the formation of a dispersed phase but solubilises glycerol in the FAME, thus ASTM level was not reached. But for the case using FAME + 0.1 and 0.2 mass% water, excellent separation results were obtained. Results of these tests show that the addition of water in small quantities (0.06 mass%), improved the % separation. The complete miscibility of glycerol and water caused the formation of larger particles and thus, two immiscible phases were formed: a water and glycerol phase, and a FAME phase. This phenomenon eased the separation of glycerol from biodiesel. Furthermore, The ASTM level was reached without methanol when 1% soap and 0.06% of water was added. The DLS measurement also indicated that the true phase separation occurred between 0.06 and 0.1 mass% as the particle size increased 10-fold in this range. The authors used gas chromatography according to ASTM D6584 to analyze the free glycerol content in the feed, retentate and permeate of the membrane system. The results obtained revealed the low concentrations of water had a great effect in the removal of glycerol from biodiesel even at 0.08 wt.%. The authors concluded that the size of the distributed glycerol phase was increased by water in the untreated biodiesel resulting to its ultra-filtration membrane separation. They found that application of membrane technology for the removal of free glycerol from biodiesel used 2.0 g of water per liter of treated biodiesel (0.225 wt.% water) against the current 10 L of water per liter of treated biodiesel. The process had avoided formation of emulsion with great decreased in loss of esters. The authors recorded excellent results in the removal of glycerol from biodiesel via membranes compared to conventional glycerol removal from biodiesel. In another study, Saleh et al. [110] investigated the effect of different levels of the components such as water, methanol, soap, and glycerol of the FAME phase (i.e., water, methanol, soap, and glycerol) on particle size of polyacrylonitrile (PAN). The addition of water to FAME mixture served to decompatibilized the glycerol and increased its particle size. At the same time, the addition of methanol acted in the opposite manner by enhancing the solubility of glycerol in FAME and reducing the particle size. The addition of soap caused a reduction in particle size by stabilizing more particles and thus, resulted in smaller particles. The authors noted that the addition of small amounts of water was found to improve the removal of glycerol from FAME, and a glycerol content as low as 0.013 mass%, well below standard of 0.020 mass%, was achieved. They observed that membranes can provide solutions for many environmental problems by recovering useful products, treating effluent streams and minimizing their harm to the atmosphere. Similarly, Cao et al. [69] noted that the final biodiesel product obtained via membrane system met the ASTM D6751 standard, which compels the free glycerol content to be less than 0.02 wt.% and the total glycerol content to be less than 0.24 wt.% respectively as shown in Table 5. Low and Cheong [114] stated that membrane

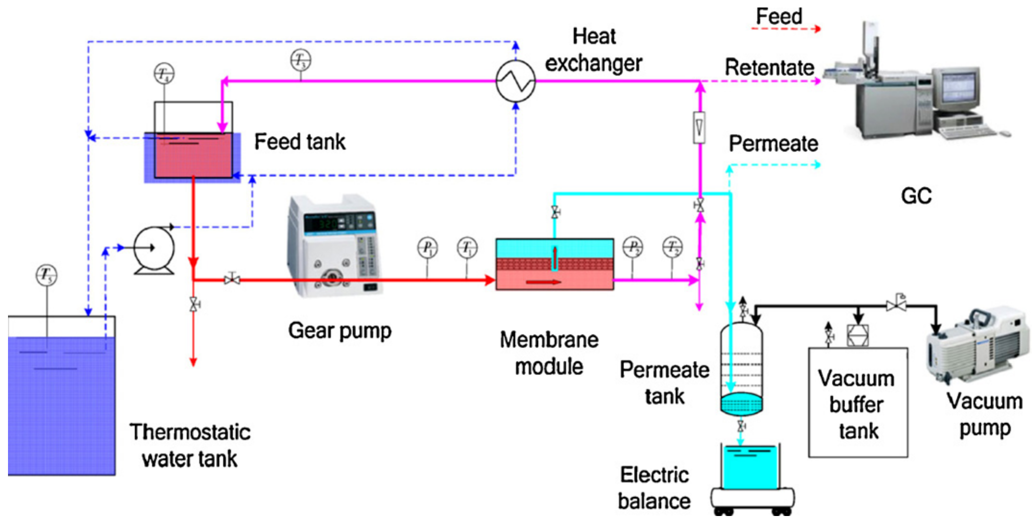

Fig. 6. Schematic diagram of the membrane separator for the biodiesel system.

filtration is a method that may improve the process of separation and purification of crude methyl ester by increasing biodiesel yield, reducing water consumption, and generating less waste materials. The authors reported improved biodiesel yield with less water use. Therefore, development and application of membrane technology to refine crude biodiesel process could be environmentally valuable, lower the energy consumption and decrease losses of alkyl esters [115].

3.2.2. Biodiesel separation through micro-filtration process

Wang et al. [2] developed a ceramic membrane separation process to refine biodiesel. The crude biodiesel produced from refined palm oil was micro-filtered by ceramic membranes of the pore size of 0.6, 0.2 and 0.1 μm. The membrane pore size 0.1 μm was most suitable and was used at different transmembrane pressures between 0.05 and 0.20 MPa and temperatures of 30, 40, 50, 60, 70 °C. The authors micro-filtered 10 kg of crude biodiesel using membrane pore size of 0.1 μm at transmembrane pressure of 0.15 MPa and at a set temperature of 60 °C. The pump was stopped when the volumetric concentrated factor reached 4. The flux of permeate was automatically recorded by the flow meter at each 3 min. After each run the membrane was rinsed by the methanol. For the process of biodiesel microfiltration by membrane pore size of 0.1 μm, the flux was quite stable over 300 $L\,m^{-2}\,h^{-1}$ because of low contents of soap and free glycerol in the crude biodiesel. The content of free glycerol, potassium, sodium, calcium and magnesium in the permeate were reduced to 0.0108% (below ASTM6751 and EN14214 stipulated value (0.020%)), 1.40 mg/kg, 1.78 mg/kg, 0.81 mg/kg and 0.20 mg/kg (below EN14538 specifications), respectively. The authors obtained high-quality biodiesel product and noted decrease in use of water needed in the conventional water washing process. In another study, Gomes et al. [92] reported that the quantity of molecular glycerol and free glycerol dissolved in biodiesel is a vital factor in the quality control of biodiesel. Therefore free glycerol in biodiesel fuel must be less than 0.02%. The authors experimented ceramic membranes with pore diameters of 0.2, 0.4, and 0.8 μm and efficiently separated biodiesel and glycerol. The preliminary results showed the prospects of membrane technology to improve the process of biodiesel separation. The authors highlighted the importance of transmembrane pressure during biodiesel refining process. Additionally, membrane with pore diameter of 0.2 μm at 2.0 bar provided best performance which gave a stable permeate flux of 78.4 kg/hm^2 and glycerol retention of 99.4% as shown in Table 6 [92].

Similarly, Murphy et al. [90] employed micro-filtration technique to determine the stability and effectiveness of different polymeric membranes for the removal of residual glycerol and water from biodiesel. These membranes include among others: polycarbonate (GE osmonics), fluoropore (millipore), SUPOR-200 (Gelman science), polypropylene (GE osmonics) and GS filter type (millipore). They observed that the recovery of biodiesel in permeates solution could possibly be due to interaction between the hydrophobic membranes and non-polar biodiesel. Both fluoropore (millipore) and GS filter type (millipore) provided biodiesel with glycerol less than 0.02% (ASTM limit). The authors stated that transmembrane pressure was instrumental for the separation of water from biodiesel and preliminary results showed that biodiesel can be efficiently purified via polymeric membranes. However, Choi et al. [116] reported that micro-filtration membrane process is more easily fouled than the ultra-filtration membrane

3.2.3. Biodiesel separation through pervaporation process

Pervaporation is also used for the purification of crude biodiesel. This membrane process is useful in effectively removing alcohol from biodiesel fuel. Shao and Huang [117] reported that pervaporation is an efficient membrane process for liquid separation. The

Table 5
Composition of the biodiesel-rich phase and methanol/glycerine-rich phase of permeate samples from different lipid feedstocks.

Lipid feedstock	Composition of the FAME-rich phase (wt.%)				Composition of the methanol/glycerine-rich phase (wt.%)			
	Biodiesel	Glycerine	DG	Methanol	Biodiesel	Glycerine	Methanol	DG
Soybean	86.36	N.D.	0.13	13.51	11.32	12.97	75.72	N.D.
Canola	84.21	N.D.	0.20	15.59	14.53	11.96	73.51	N.D.
Palm	82.47	N.D.	0.50	17.03	18.39	9.28	72.33	N.D.
Yellow grease	79.07	N.D.	0.38	20.55	19.06	7.73	73.21	N.D.
Brown grease	83.42	N.D.	0.41	16.17	15.41	11.38	73.21	N.D.

N.D. ¼ not detectable.

Table 6
Steady-state permeate flux and glycerol retention values for membranes with 0.2, 0.4, and 0.8 μm pore diameter at 1.0, 2.0, and 3.0 bar and T = 60 °C.

Average pore diameter (μm)	Pressure (bar)	Permeate flux (kg/hm^2)	Glycerol content in permeate (mass%)	Glycerol retention (%)
0.2	1	12.2	0.04 ± 0.004	99.6
0.2	2	78.4	0.06 ± 0.009	99.4
0.2	3	56.1	0.06 ± 0.005	99.4
0.4	1	52.2	0.05 ± 0.003	99.5
0.4	2	83.6	0.07 ± 0.015	99.3
0.4	3	60.0	0.10 ± 0.010	99.0
0.8	1	36.0	0.06 ± 0.008	99.4
0.8	2	46.3	0.08 ± 0.010	99.2
0.8	3	41.3	0.10 ± 0.016	99.0

Table 7
Advantages of membrane technology over conventional technologies in the field of biodiesel refining.

Mode of refining	Impurities removal	Purity/quality	Amount of water use	Energy consumption	Time required	Waste disposal	Reference
Wet washing	Difficult costly	Purity of 99%	Huge amount of water, H_2SO_4 and petroleum ether	High energy consumption	High time requirement	Huge wastewater disposal	[16,44,119–122]
Dry washing							
Magnesol ion exchange resin	Less cumbersome product	High-quality	Waterless consumption	Low energy	Less time required	Less waste disposal	[96,99]
Membranes	Less difficulty	Better quality product	Little amount of water	Less energy consumption	–	Generated less waste, reduced effluent quantity	[2,71,92,113,114]

authors reviewed the opportunities, and the prospect of pervaporation in membrane separation. Van Gemert and Petrus Cuperus [118] reported that polymeric pervaporation membranes sometimes show great variety in performance when they are alternately used for different solvent mixtures. Nick [100] remarked that one of the most promising uses of pervaporation is the removal of methanol from transesterified products. The authors noted that methanol forms azeotropes with many methyl esters, so driving out methanol also removes a reactant. As a result, separation of these azeotropic mixtures via conventional distillation and evaporation is difficult. Therefore polymeric membranes with low degree of linkages can be engineered which will preferentially permeate methanol.

In summary, Table 7 presents the advantages and disadvantages of different technologies for the purification of crude biodiesel.

3.3. Biodiesel purity via membrane refining

The use of membranes to refine crude biodiesel product has been remarkable, producing biodiesel purity of 99% [46]. Cao [88] stated the glycerol content of biodiesel produced using membrane reactor is significantly lower than that produced through a traditional batch reaction. Also, membrane extraction technique was found to provide about 90% purity of biodiesel [97]. Cao et al. [69] reported the biodiesel produced was of excellent purity without any confirmation of the presence of particulate matter.

4. Conclusions and recommendations

Based on the investigations carried out from published researches of several numbers of engineers and researchers, the following conclusions and recommendations were made:

1. Membrane reactor was observed to restrict the passage of unreacted oils to biodiesel product mixture, hence providing high-quality biodiesel fuel.
2. Membrane reactor was found to be capable of processing low quality feedstocks such as yellow grease.
3. Application of alkaline catalyst in membrane system for the production of biodiesel was found to produce soap while acid catalyst though avoided soap formation but slow reaction rates were observed.
4. Leaching of solid alkaline catalyst was observed but the process provided high conversion of triglyceride to esters.
5. Ultrafiltration and microfiltration membrane processes were found to perform very well in the removal of impurities such as glycerol, catalysts and soap from biodiesel, whereas pervaporation process was ranked among the most promising technologies for the removal of methanol from biodiesel.
6. Membrane biodiesel production process was reported to give product whose properties met ASTM standard specification.
7. To achieve high biodiesel yield via membrane reactor operation, development of cheap and very active heterogeneous catalysts is necessary.
8. Membranes need to be maximally harnessed for their unique characteristics of high available surface area per unit volume, high selectivity/conversion, capacity to control components contact between two phases that is rare with conventional systems, ability to recover important products, treat effluents and minimize their harm to the atmosphere.
9. More research should be conducted to study the fouling effects and stability of the membranes for the production and refining of biodiesel.

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